Study of the heavy metal content of floodplain soils along the upper Tisza River by sequential BCR extraction in Hungary

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Abstract

In this study PTEs, [potentially toxic elements (Cr, Cu, Mn, Ni, Pb, and Zn)] were investigated in the upper layer of floodplain soils that occurred as a result of accident in the area of two mine tailings in Northwestern Romania. A large amount of sediment was deposited on the soil of floodplains along the Hungarian section of River Tisza, which could represent a threat to the environment. Floodplain soil samples were collected from four locations in Hungary from an area of the river stretching to about 250 km. BCR (Bureau Communautaire de Référence) sequential extraction method was used to analyze both post-flood and present samples. Most of the analyzed elements (Cd, Cr, Cu, Ni, Pb, Zn) were found in the residual fraction, but there is a notable soluble amount in hydroxylammonium chloride extractable fraction. The results allow a comparison of the changes that have taken place over time, in addition to serving as a basis for further studies.

Keywords: potentially toxic element, sequential extraction, flood waves sediments, floodplain, Tisza River

Introduction

Twenty years have passed since two successive specific contamination (cyanide solution and heavy metal-containing sludge) waves hit River Tisza in the spring of 2000 (WWF, 2000; UNEP/OCHA, 2000; BURNOD-REQUIA, 2004; BLACK & WILLIAM, 2001). This river originates in the Carpathians (Romania and Ukraine) and it also collects Eastern Slovakian rivers in Hungary, then flows into the Danube in Serbia after passing through lowland areas. Accordingly, the mining (Pb, Zn, Ag, Au) and industrial activities of several countries have an impact on the water quality of River Tisza (BIRD et al., 2003; BREWER et al., 2003). Among these activities, the most important ones are those that discharge dissolved substances into the river (MACKLIN et al., 2003; KRAFT et al., 2006) in addition to discharging sediments with particles of different sizes. Several results have already been reported on the effects of pollution associated with these heavy floods in the above year. The first studies were directed at understanding the short-term but highly destructive impact of

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cyanide (SOLDÁN et al., 2001; KONCSOS & FONYÓ, 2004) in the Upper-Tisza areas of Hungary. The study on the additional effects of the flooding included the monitoring of floodplain soils (BALOGH et al., 2017; SZABÓ et al., 2008, 2010), oxbows, their waters and sediments (FLEIT & LAKATOS, 2003; BABCSÁNYI et al., 2019) and certain elements of the soil-plant system (As, Cd, Co, Cu, Fe, Ni, Pb, Zn) in the given area (GOSZTONYI et al., 2010). The results of these studies were published in various journals (ALAPI & GYŐRI, 2003; HELTAI et al., 2018; ÓVARI et al., 2004). The above issue was also investigated in a collaboration of a wide circle of researchers with funding from National Science Foundation (USA) and Hungarian Academy of Sciences also resulting in publications (ADRIANO et al., 2003). Among the results, those related to the element content of floodplain soils can be highlighted, because by settling down after the floods the sediment containing potentially toxic heavy metals created a new soil layer in the floodplains. According to the data of the 0–300 cm soil layer studied by LAKANEN-ERVIÖ (1971) and aqua regia or strong nitrit acid extraction, it can be stated that such an event has occurred several times in the floodplain of River Tisza during the last more than two thousand years (NGUYEN et al., 2009; O'SHEA, 2011; PROKISCH et al., 2009). The floods of 2000–2001 formed a new top layer with a thickness of several centimeters in the Upper Tisza floodplains, which exhibits higher element content than the previous surface (GYŐRI et al., 2015). Although the use of this area is mostly limited to forests (dominantly *Salix alba, Salix fragilis, Robinia pseudoacacia*), grazing animals, and to a smaller extent arable land (winter wheat, maize) and possibly oxbows and fishing lakes, the issue of food safety cannot be overlooked either. For this reason, it seems reasonable to continue the examinations. In the meantime, several changes have taken place, as the Cu, Cr, Fe, Mn, Ni, Pb, and Zn content of the River Tisza sediments were measured in Serbia using a modified Tessier method (SAKAN et al., 2007, 2009; TESSIER et al., 1979), and the results of Ukrainian researchers were also published (LINNIK et al., 2017). As a result, an almost comprehensive description about the condition of River Tisza was given by the researchers dealing with the topic using the applied methods. However, there is one issue that could not be examined in sufficient detail. Related to this issue we actually need to detect the chemical forms of the heavy metals found in the floodplain sediment. One reason for this is that these methods are quite time-consuming and labor-intensive while the other reason is that the BCR-SEP (BCR sequential extraction) procedure has since become generally accepted (SUTHERLAND, 2010; ZIMMERMAN & WEINDORF, 2010; ZHANG et al., 2009; BO et al., 2014; MADEJÓN et al., 2018; JOKSIC et al., 2005; SUNGUR et al., 2014). When the research group led by the first author of this paper began working on this topic, it was only possible to use the method developed by MCGRATH & CEGARRA (1992). Which method was used by the first author of this paper acquired as a result of his research work in Rothamsted Research. Other results were published for the 0–300 cm soil layers of our sampling sites as well (ADRIANO et al., 2003; GYŐRI et al., 1996). Today out of all the methods, analyses that can be used to estimate the amount of potentially toxic elements in different compound forms are of outstanding importance in researches worldwide. Now, however, Authors had to face the fact that BCR has become the most common method, which is successfully used by researchers to study

soils, sewage sludge, sediments (fresh and salt water), and dust (FERNÁNDEZ-ONDONO et al., 2016; YONGFENG et al., 2008; SUN et al., 2015; ASTATKIE et al., 2021; CASALINO et al., 2013; PUEYO et al., 2008; HORVÁTH et al., 2010; WEI & YANG, 2010; ARENAS-LAGO et al., 2014; MATABANE et al., 2021; BERAR SUR et al., 2012; ONDOÑO et al., 2017; MASSOLO et al., 2012).

Based on the situation described above, we decided to determine the soluble element content of the samples by re-measuring the archived ones and by taking new samples, using the BCR method. In this article the results of measuring Cd, Cr, Cu, Ni, Pb and Zn content are reported. With this procedure two goals were set: (i) to obtain new data so that they would be available for researchers for comparison in the next decades and (ii) to detect possible changes in the condition of compounds studied over the last nearly twenty years. Of course, this period have brought changes in this area because the trees in the young forests of 2000 have since developed, there are fewer grazing animals now and the use of floodplain soils as arable land has become less common as well. In spite of these changes, this process was necessary to provide future generation an access to basic data about the event.
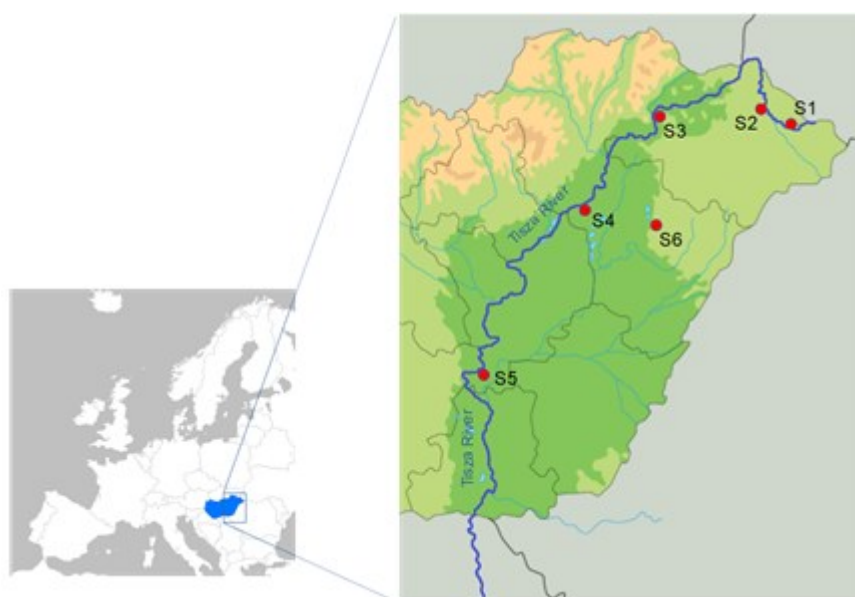

Figure 1
Map of the sampling sites

Materials and Methods

Soil samples were collected in 2000 and after the flood by deep drilling with a Nordmeyer drill (Nordmeyer Holland, Overveen, The Netherlands). We sampled the 300 cm deep soil layer in three replications (PROKISCH et al., 2009). Due to the fact that there was no significant change in the analytical data of the samples taken in

2011 compared to the sampling results in 2000, in 2017 we only sampled the top 10 cm layer of soils. Floodplain soil samples were collected from five locations in Hungary from an area of the river stretching to about 250 km (*Figure 1 and Table 1*).

Table 1
Sampling sites

Sampling sites	Geographical coordinates	River km	Type of samples	Additional information
Tivadar (S1)	N 48º 04' 00.6" E 22º 31' 04.8"	709	active floodplain	affected by the 2nd pollution event
Vásárosnamény (S2)	N 48º 07' 46.5" E 22º 19' 39.5"	683	pasture	affected by the 1st and 2nd pollution events
Rakamaz (S3)	N 48º 07' 43.8" E 21º 26' 28.7"	543	pasture	affected by the 1st and 2nd pollution events
Tiszacsege (S4)	N 47º 42' 59.9" E 20º 57' 08.7"	455	active floodplain	affected by the 1st and 2nd pollution events
Tiszakürt (S5)	N 46º 53' 14.5" E 20º 07' 17.4"	275	arboretum, nature reserve	there have been no floods since 1860
Látókép (Debrecen) (S6)	N 47º 33' 41" E 21º 27' 01"		arable crop pilot area from 1983	there has been no flood since human memory

The results of the soil samples analyses taken in the floodplain were compared not only with each other but also with the data of two other areas. One is the soil of the Tiszakürt Arboretum (S5), which is on the reclaimed side of dam but close to the river bed and has not been covered with floods since its construction (mid-19th century). The other is an experimental site with calcareous chernozem soil (111 m above sea level) belonging to the University of Debrecen. This experimental site was established in 1983 to carry out crop production experiments (NAGY, 2019). We compared the results of floodplain soil samples with data from these two areas.

Soil samples were air dried, grinded with a SK 1 type device (Retsch Gmbh Germany) and sieved (<2mm) for further analysis. The authors have used several methods over the last twenty years. Our research activity in the topic was started with a method according to the Hungarian standard (MSZ 21470-50, 1998), with HNO_3-H_2O_2 digestion, which gives total elemental contents. Then we continued with the Lakanen and Erviö method (LAKANEN & ERVIÖ, 1971) determination of the easily available metals content. Later we used the McGrath and Cegarra (MCGRATH & CEGARRA, 1992) method of sequential extraction because we had experience in this method (GYŐRI et al., 1996).

Finally, we also gained experience in sequential extraction of commonly used BCR (URE et al., 1993). *Table 2* shows the procedure steps of the BCR sequential extraction method.

In order to obtain the standard data, we used a Merck-made (E. Merck, Darmstadt, Germany) analytical grade solutions. Merck and BDH standard solutions were used to prepare the stock-solutions, and VWR (VWR International Ltd.,

Debrecen, Hungary) solid chemicals were also used. Ultrapure water was used to prepare the solutions (Millipore, Paris, France).

Table 2
The BCR sequential extraction procedure steps

Steps	Chemical information
Step 1. Extraction by 0.11 M HOAc	Exchangeable, water and acid-soluble (e.g., carbonates) species
Step 2. Extraction by 0.1 M NH_2OH – HCl (pH=2)	Reducible (e.g., Fe/Mn oxides, oxihydroxides) species
Step 3. Extraction by 8.8 M H_2O_2 + 1 M NH_4OAc (pH=2)	Oxidable (e.g., bound to organic matter or sulfides) species
Step 4. Extraction by aqua regia	Residual fraction

Samples were analyzed using an Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) (Perkin-Elmer Optima 3300 DV; Perkin-Elmer Ltd., Shelton, USA) and an X7 ICP-MS (Thermo Fischer Scientific) in 2018 too (KOVÁCS et al., 1998, 2000).

Target analytics were Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S and Zn. In this study, we focused on the Cd, Cr, Cu, Ni, Pb and Zn elements because these elements had connection to the contamination on floodplain. Certified standard materials used in QA/QC were BCR CRM 141R: calcareous loam soil; BCR CRM 142R: light sandy soil for and BCR CRM 143R: sewage sludge amended soil (QUEVAUVILLER et al., 1996; MAIER et al., 1994).

The pH of the soils in distilled water (DW) and 1 ml^{-1} KCl solution was also measured.

The sample treatment and metal analyses were done in a laboratory accredited by the National Accreditation Body of Hungary (member of the European Accreditation). For quality insurance, the laboratory regularly participates in interlaboratory comparisons for testing metal analyses in soils and sediments. In-house standards were regularly used, too.

The data collected from several locations in Hungary were used to evaluate the differences among sampling times and locations. The basic statistical parameters (mean, standard deviation) were determined, which was followed by an one-way analysis of variance (ANOVA) to evaluate significant differences across sampling times. Differences in variance among sampling years were compared using the Duncan test at the significance threshold of $P<0.05$. All statistical analysis was performed by using SPSS Statistics 27.0 (SPSS, Inc., Chicago, IL, USA).

Results

For the discussion of measurement results, we consider it essential to briefly characterize the medium (soil) from which samples were taken in the floodplain area. River Tisza and its tributaries are characterized by the building of dams and the

cutting off river meanders during the river regulation, which began in 1846 in order to prevent the destruction caused by the river. From this time on, the river settled the sediment of floods in between the dams. As a result of this process, the area between the dams changed to a varying extent from flood to flood every year.

Thus, sampling in the floodplain area shows a specific soil structure that differs from the structure of soil layers outside the dam area. Here there is only a thin top layer (0–10 cm) interwoven with the roots of the undergrown vegetation of the pastures or forests. The other layers do not show the characteristics of traditional soil profiles, only the types of sediments (sand, clay, loam). There are earthworms only in the top soil layer. The decomposing remnants of the buried grasses that formerly grew on the soil can be observed in several areas in the 0–30 cm layer. After each flood, a new layer of sediment of various thickness was settled on the surface creating a new surface for vegetation and for the researchers to study following the flood has been withdrawn. This process is well illustrated in the photographs where these new layers are visible. This phenomenon did not always make sampling and analysis easier, as the particularly intensive flow of water during the floods made the distribution of contaminants in the new soil layers inhomogeneous.

When studying the data, the first question to arise is to what extent the pH of the topsoil layer has changed, because the change in the solubility conditions of the elements may be dependent on it. Regarding the pH values of the samples from the different sampling sites, it can be determined that the values measured at Tivadar (S1) and the values measured in the distilled water were between 6.66 and 6.26, while in the 1M KCl they were between 6.17 and 5.40. This value ranged from 6.82 to 6.25 and it was found 6.36 to 6.11 at Vásárosnamény (S2) and 7.0–6.51 and 6.33–5.98 at Rakamaz (S3). At Tiszacsege (S4) they were between 7.07–6.66 and 6.71–6.43. Comparing these values with the data of Látókép (S6) experimental site (S6), it can be concluded that on a chernozem soil the pH is between 7.2 (H_2O) and 6.2 (KCl), which shows a wider range than in the Tisza floodplain. No significant differences were found between floodplain values over time. There is only a slight difference between the data of the different locations, as the pH values are slightly lower in Tivadar (S1) and Vásárosnamény (S2).

The presentation of the results with the location has been started closest to the source of the contamination. First, in the description of the results of the first years (2000) were compared with the result of the recent sampling for the elements Cd, Cr, Cu, Ni, Pb, and Zn. The results of the variance analysis (*Table 3*) show that there has been no statistically significant change at Tivadar (S1), which received only the second wave of sediment contamination over the past nearly twenty years.

In contrast, in the case of several elements (Cd, Ni, Pb) at Vásárosnamény (S2) (the so-called reducible elements – second step), that means the element content of the 2018 sampling with hydroxylammonium chloride extraction are significantly higher than the results of the 2000 sampling. The same effect can be observed from the ammonium acetate extract of oxidizable (third step) elements for Cr, Pb and Zn. A significant increase in the Cu content with acetic acid (first step) extraction was also observed.

These higher values can be explained by the redirecting impact of the rapid but short-lived flooding (in 2006) that took place during the studied period, because a

new 0.5–1.0 cm layer was created at the intersection of two rivers (Szamos and Tisza). However, it is noticeable that there is no significant effect on the element content values of the aqua regia extraction (residue).

Further down along the river, Rakamaz (S3) is the next site at the confluence of the Tisza and Bodrog rivers. At this area it can occur that both rivers flood at the same time. At this point, an increase in copper content can be observed in the ammonium acetate (third step) extraction. Zinc content is also statistically higher than in samples taken after the year 2000 flooding.

Table 3
Analytical and statistical results of heavy metal contents for different years and sampling sites1 in the 0 to 10 cm soil layer

Sampling Site	Year	BCR extraction	Cd	Cr	Cu (mg kg⁻¹)	Ni	Pb	Zn
S1	2000 (n=6)	Step1	0.09±0.02	1.50±0.08	1.23±0.18	4.40±0.81	2.00±0.12	4.58±0.41
		Step2	0.09±0.02	1.83±0.08	5.44±0.33	5.88±0.16	20.03±1.43	12.33±0.45
		Step3	0.42±0.02	7.48±0.60	7.38±1.11	5.65±0.32	4.43±0.72	13.76±1.24
		Residual	1.00±0.08*	46.60±2.50	40.20±4.19	39.10±1.18	20.53±1.40	86.37±2.89
	2018 (n=6)	Step1	0.09±0.01	1.49±0.09	1.11±0.08	4.01±0.42	2.02±0.03	4.73±0.48
		Step2	0.09±0.01	1.86±0.21	5.51±0.34	5.46±0.28	19.43±1.00	15.67±2.12
		Step3	0.42±0.01	7.39±0.56	7.18±0.55	5.05±0.84	4.44±0.25	13.83±2.07
		Residual	0.83±0.06*	40.07±3.62	37.83±0.80	37.43±3.26	20.17±0.83	80.27±2.98
S2	2000 (n=6)	Step1	0.46±0.01	1.55±0.12	1.41±0.12*	4.51±0.40	2.65±0.18	40.43±4.90
		Step2	0.22±0.03*	3.01±0.28	13.71±1.51	6.31±0.17*	44.53±1.95*	101.30±11.40
		Step3	0.44±0.02	8.28±0.29*	7.93±0.78	7.88±0.28	6.96±0.14*	30.41±2.88*
		Residual	0.44±0.04	59.27±3.60	67.93±10.38	24.80±3.90	97.13±9.86	202.00±8.89
	2018 (n=6)	Step1	0.42±0.02	1.52±0.09	3.03±0.15*	4.58±0.19	2.93±0.21	36.23±1.80
		Step2	0.28±0.01*	3.31±0.28	14.33±0.21	9.48±0.09*	57.23±3.31*	102.13±8.36
		Step3	0.43±0.01	9.38±0.32*	8.80±0.33	8.08±0.20	8.16±0.05*	36.27±0.50*
		Residual	0.42±0.07	61.80±2.49	68.00±1.56	28.43±3.33	96.73±8.36	207.33±11.68
S3	2000 (n=6)	Step1	0.26±0.01	1.41±0.03	1.84±0.10	4.36±0.55	2.54±0.09*	19.33±0.72*
		Step2	0.10±0.01	2.81±0.09	11.73±0.61	7.34±0.33	42.20±2.10	63.07±1.48
		Step3	0.44±0.01	8.88±0.19	6.77±0.28*	7.47±0.24	6.57±0.17	30.20±1.34
		Residual	1.91±0.13	41.47±2.03	21.13±1.81	10.84±0.41	111.60±10.33	135.00±18.52
	2018 (n=6)	Step1	0.27±0.02	1.46±0.06	1.82±0.06	4.97±0.18	2.57±0.04*	23.47±2.18*
		Step2	0.09±0.01	2.43±0.35	11.30±0.95	6.99±0.20	42.13±2.45	64.47±4.21
		Step3	0.42±0.02	8.51±0.51	7.49±0.31*	7.68±0.46	6.54±0.19	28.77±3.05
		Residual	1.64±0.19	43.60±3.08	22.60±2.65	11.67±1.56	114.33±8.74	136.00±16.52

Table 3 cont.

S4	2000 (n=6)	Step1	0.43±0.06	1.41±0.12	2.14±0.23	4.40±0.40	2.70±0.10	53.87±2.01
		Step2	0.09±0.01	2.39±0.03	13.57±0.87	5.85±0.17	26.07±0.57	87.20±8.23
		Step3	0.45±0.06	7.71±0.46	5.98±0.65	4.37±0.25	3.76±0.20	22.20±1.59
		Residual	1.45±0.14	32.57±2.12	43.97±4.67	22.47±3.83	21.77±1.85	128.00±3.61
	2018 (n=6)	Step1	0.45±0.05	1.46±0.11	2.22±0.29	4.48±0.36	2.68±0.11	51.10±3.60
		Step2	0.09±0.02	2.37±0.14	12.90±0.62	5.95±0.05	24.83±1.06	84.70±1.55
		Step3	0.45±0.06	7.72±0.20	5.65±0.58	4.48±0.59	3.84±0.17	22.47±1.59
		Residual	1.48±0.19	30.97±0.60	44.50±3.17	23.50±1.22	21.37±2.58	129.67±18.56
S5	2000 (n=6)	Step1	0.19±0.01	1.65±0.05	2.35±0.18	5.06±0.36	1.20±0.08	3.20±0.21
		Step2	0.09±0.01	2.40±0.17	6.30±0.23	4.89±0.27	11.2±0.97	12.60±1.33
		Step3	0,15±0.02	6.85±0.22	7.46±0.26	4.95±0.29	3.3±0.22	8.88±0.36
		Residual	0.72±0.08	26.2±2.90	10.95±0.78	22.3±1.95	16.20±1.06	48.80±2.76
	2018 (n=6)	Step1	0.16±0.02	1.55±0.58	2.12±0.12	4.51±0.27	1.92±0.06	3.15±0.24
		Step2	0.10±0.01	2.23±0.12	6.63±0.22	5.04±31	10.97±0.87	11.53±1.21
		Step3	0.12±0.02	6.45±0.19	6.65±0.27	4.48±0.37	3.1±0.17	7.17±0.34
		Residual	0.70±0.07	24.90±2.77	12.50±0.81	20.7±1.86	17.10±1.69	50.40±2.92
S6	2000 (n=6)	Step1	0.17±0,02	1.45±0.07	2.66±0.14	2.21±0.19	0.48±0.06	2.11±0.04
		Step2	0.09±0.01	2.43±0.14	8.97±0.24	4.32±0.21	12.14±1.11	8.32±0.29
		Step3	0.13±0.01	6.13±0.21	5.15±0.22	1.35±0.09	2.69±0.16	7.08±0.31
		Residual	0.70±0.06	21,12±2.15	4.86±0.21	14.98±1.54	7.31±0.54	54.43±3.02
	2018 (n=6)	Step1	0.16±0.02	1.42±0.06	2.84±0.17	2.19±0.16	0.50±0.08	2.09±0.05
		Step2	0.10±0.01	2,41±0.16	8.45± 0.24	4.64±0.023	11.2± 0.94	8.83±0.32
		Step3	0.12±0.01	5.88±0.17	5.44±0.23	1.12±0.09	2.71 ±0.05	6.52±0.30
		Residual	0.68±0.08	20.7±1.98	5.36±0.28	14.20±1.38	6.59±0.23	55.80±3.18

Data shown are means for all tested samples ± SD, the numbers followed by stars indicate significant differences (P<0.05) for each element among sampling years.

Tiszacsege (S4) is the site where two additional rivers Sajó and Hernád, originating in Eastern-Slovakia, flow into the Tisza. At this site, no significant effect was found for any of the used extracts.

In order to provide basic data on the sampled areas with the commonly used BCR sequential extraction method, the ratio of the investigated elements are shown in *Figure 2*.

In addition, by summarizing the data, the proportions of the data for all element contents obtained with the different extraction steps can be determined.

Accordingly, the solubility of the cadmium content of the floodplain samples shows varying trends. The total cadmium content is lower than 2 mg kg^{-1} at the two control areas and at Tivadar (S1) and Vásárosnamény (S2) as well. At the two other sample-taking sites it is close to 2.5 mg kg^{-1}. The results gained with the first two

extractants are the same at Tivadar (S1) while the result for the third step corresponds to the results of the floodplain samples (0.4–0.45 mg kg^{-1}).
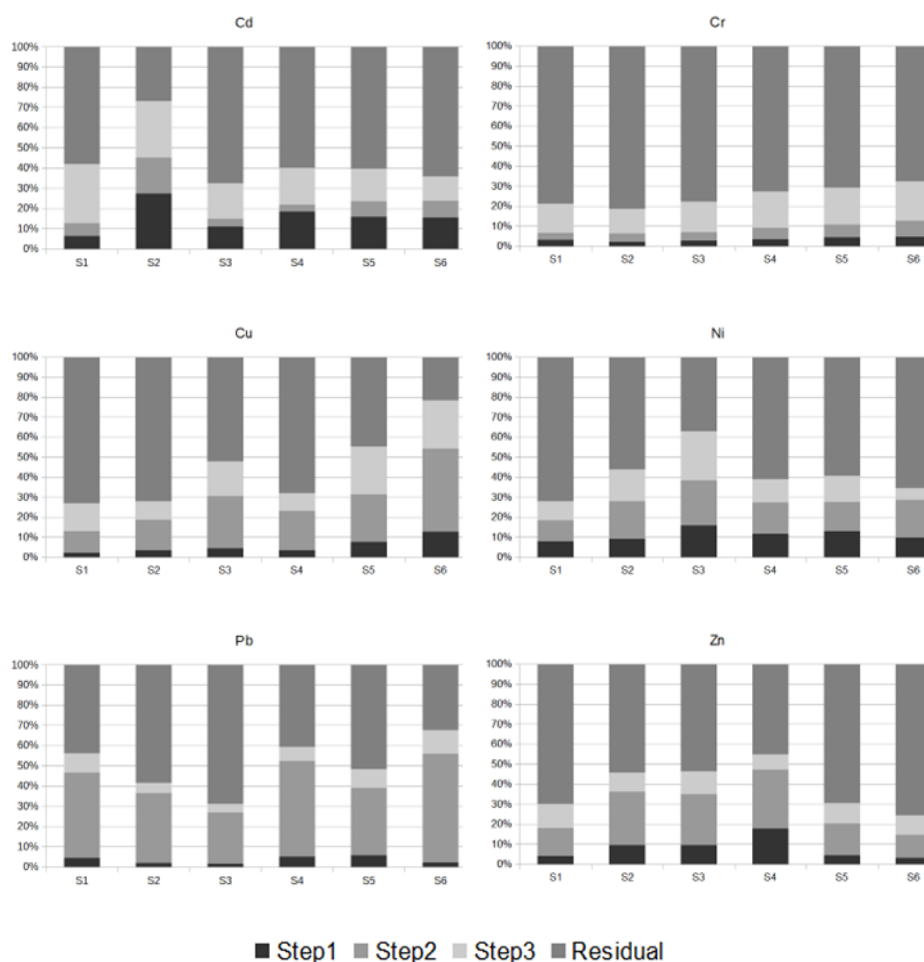

Figure 2
The geochemical fractionation of heavy metals.
The colors represent the steps of BCR extraction

The amount in the first, third and fourth extractants is almost the same with 27% at Vásárosnamény (S2). The second (hydroxylammonium chloride) extractant removes 18% of the total amount of cadmium. At this sampling site, the amount of cadmium extracted with aqua regia (residue) is the smallest compared to the other sampling sites. There is no significant difference between the results of the four floodplain sites.

The cadmium result obtained with the third extraction is the lowest in the control samples while the residue values range from 60.5 to 64.2% (S5, S6). It is noticeable that the value of the remaining fraction is only 27.1% at Vásárosnamény (S2) and 67.8% at Rakamaz (S3).

In terms of chromium, it can be stated that the total amount in the Tivadar (S1) and Vásárosnamény (S2) samples is 50.8 mg kg^{-1} and 76.0 mg kg^{-1}, while at Rakamaz (S3) it is 56.0 mg kg^{-1} and Tiszacsege (S4) it is 42.5 mg kg^{-1}. In the samples of the two areas reclaimed of floods, the samples were 35.1 mg kg^{-1} and 31.3 mg kg^{-1}.

During dissolution, the first stage acetic acid (first step) extraction contained 2–3% of the total amount at Tivadar (S1) and Vásárosnamény (S2), while at Rakamaz (S3) it was 2.6% and 3.4% at Tiszacsege (S4). In the reclaimed area, this rate is more than 4.4%. In the second extraction it was between 3.7 and 5.6% of the total amount at Tivadar (S1) and Tiszacsege (S4), while in the samples of the reclaimed area this value was 6.4–7.8%. The third extractant has already dissolved more than 10% of the total amount. In the case of floodplain samples, the proportions range from 12.3% at Vásárosnamény (S2) to 18.2% at Tiszacsege (S4), while on the reclaimed area they are 18.4–19.6%. The proportions of soluble elements in aqua regia extraction (residue) varied between 81.1% and 70.4% (Vásárosnamény (S2) and Tiszacsege (S4)), while the two control areas differed only slightly with 70.9% [Tiszakürt (S5)] and 67.5% [Látókép (S6)].

There are significant differences in the total copper content results, as the values in the two control areas are significantly lower with values ranging from 27.9 to 21.4 mg kg^{-1}. The amount of copper was the highest in the Vásárosnamény (S2) samples with 94.2 mg kg^{-1}, in samples from Tivadar (S1) it was 51.6 mg kg^{-1}, at Rakamaz (S3) it was 45.1 mg kg^{-1} and at Tiszacsege (S4) it was 65.3 mg kg^{-1}. The proportion of acetic acid (exchangeable and week acid soluble soluble) extract is the highest in the Látókép (S6) samples (12.4%) and lowest in the Tiszakürt (S5) samples (7.6%). The copper content measured with acetic acid extract in the other sites is even lower (2.2–4.2%).

The total nickel content of the Tivadar (S1) and Vásárosnamény (S2) samples is almost the same (51 mg kg^{-1}). Lower amounts were measured at Tiszacsege (S4) (38 mg kg^{-1}), Rakamaz (S3) (31 mg kg^{-1}) and Tiszakürt (S5) (34 mg kg^{-1}). The nickel content is the lowest at Látókép (S6) site with 23 mg kg^{-1}. The extraction rates are characterized by the fact that the acetic acid extract already contains 7–16% of this element, depending on the location. The ratio was the lowest at Tivadar (S1) and the highest at Rakamaz (S3). For the second extractant (reducible), the values ranged from 10 to 22%, the values of the two control areas showed average values among the sites (14–19%). The ammonium acetate (third step) solution dissolved 9.6% of nickel from the floodplain samples at Tivadar (S1) followed by 16% at Vásárosnamény (S2) and 24.5% at Rakamaz (S3). The smallest amount with this extractant was measured for Látókép (S6). Similarly to copper, Rakamaz (S3) sample showed the lowest result with 37% acquired by aqua regia extraction among the floodplain samples, while the result for Tivadar (S1) exceeded 70%. This means that here the ratio of the other two extracts is barely 10%.

In the former or operating mines in the drainage basins on upper part of the River Tisza, mining activity was directed at extracting ores containing gold, silver, zinc and lead. Thus, the latter two elements also appeared in the mine waste drainages. For our study this means that both Vásárosnamény (S2) and Rakamaz (S3) showed 165 mg kg^{-1} of total lead content. However, the proportions are slightly different, with values 25.5% at Rakamaz (S3) and 35% at Vásárosnamény (S2). This difference can also be seen in the aqua regia extraction, as 59% was measured at Vásárosnamény (S2) and 69% was at Rakamaz (S3). Lead content is about 50 mg kg^{-1} at Tivadar (S1) and Tiszacsege (S4). At Tiszakürt (S5) this value is lower with 22.6 mg kg^{-1} and it is even lower at the soil in Látókép (S6) experimental site. The proportion of soluble acetic acid is around 1.5-2.0% at Vásárosnamény (S2), Rakamaz (S3) and Látókép (S6), while it barely exceeds 5% at the rest of the sites. This element represents a significant proportion in the second extractant, as this value is more than 40% at Tivadar (S1), it decreases to 35% at Vásárosnamény (S2) and 25.5% at Rakamaz (S3). It reaches 47% at Tiszacsege (S4), which may indicate the emergence of another type of lead-containing sediment. Of the two control areas, the proportion is 33% in Tiszakürt (S5) and the highest proportion was observed with 54% at the Látókép (S6) experimental site. This means that more than 12 mg kg^{-1} of the total 22.6 mg kg^{-1} belongs to the reducible fraction. With the third extractant, the proportion of lead (oxidisable) does not reach 10% in the floodplain samples, but at Rakamaz (S3) it does not even exceed 4%. It is noteworthy, however, that the values measured for the two control areas in Tiszakürt (S5) are similar to the results measured at Tivadar (S1) (9.6%), and these values are near 12% at Látókép (S6).

According to our measurements, zinc is the element which arrived in large quantities with the solid material transported by the two waves of flooding and spread on the floodplain of River Tisza. The total zinc content at each location where both waves of flooding passed through were much higher than in the two control areas. While at Tivadar (S1) the total measured amount is only 114 mg kg^{-1}, on the other side, it is 382 mg kg^{-1} at Vásárosnamény (S2), 253 mg kg^{-1} at Rakamaz (S3) and 288 mg kg^{-1} at Tiszacsege (S4). For these values, the total zinc content of the two control areas is very low with 70 mg kg^{-1} (*Table 2*). In the case of the acetic acid extraction, the samples of non-contaminated areas account for 3.0-4.5% of the total zinc content, and the data are similar in Tivadar (S1). However, in the samples of Vásárosnamény (S2) and Rakamaz (S3) it is more than 9%, while at Tiszacsege (S4) it exceeds 17%. The results of the second extractant shows similar results to that of the first extractant, but the proportions here are about twice as high as for the former one, but the result at Tiszacsege (S4) are not significantly different. The results are between 8–12% in case of the third extractant, where the extraction rate exceeds 10% at Tivadar (S1) and Rakamaz (S3). The aqua regia extraction is between 70 and 76% for the two control areas and Tivadar (S1), and it resulted 54 and 45% for the other location (*Figure 2*).

Discussion

The applied BCR could be used to properly separate and determine the potentially toxic elements from the newest upper layers of the Tisza floodplain. These layers turned form being a floodplain sediment into a specific type of soil over a short period of time since its structure, composition, physical and chemical properties make it into a unique soil construction. At the same time, it must be considered as a potential source of danger. For this reason, it is essential to collect as much information about it as possible. Part of this effort is to examine it with a widely used method. In comparison with our previous data, we have significantly more detailed information than before (GYŐRI et al., 2003). This is the case especially in terms of acetic acid-soluble fraction, as its proportion in floodplain soils exceeds 5% for several elements (Ni, Pb, Zn). The publication of the analysis data of the calcareous chernozem soil at Látókép (S6) site and the comparison of them with the data of the other samples can be considered a completely unique approach and the application of this method is recommended for the complex study of the long-term effects of fertilization, irrigation and tillage.

According to OSÁN et al. (2002, 2007) the determination of the mineral components of the sediments contaminating the area by powder diffraction and electron probe microanalysis led to the conclusion that lead, zinc and copper elements characterize the studied sediment. These elements are predominantly bound to pyrite (pyrite) and zinc sulfide (ZnS). This also explains our research results regarding the high proportion of reducible fraction outside the residue.

An exciting issue may be how the proportion of elements in the fractions extracted from the soils can change when the soils have low buffering capacity and neutral pH. Experiments were performed by GOSZTONYI et al. (2010) to address this question investigating the effect on the amount of Zn in the range between 0.001 to 0.1 M HNO_3 in an artesian sample taken from an area close to Tivadar (S1). The 0.1 M HNO_3 solution was found to dissolve 15 times more zinc than the dilute solution. These results are consistent with our finding about the pH of the floodplain soils not having changed over the past nearly twenty years. However, it is very important to monitor the pH of such soils until a decrease in the values occurs. The sequential BCR method for which basic data are available should be used subsequently. It seems reasonable to integrate these data into regional data collection that allows informed decisions to be made in such cases.

Comparing our results with the results of BABCSÁNYI et al. (2019) it can be determined that they found a higher proportion of residue fractions in the riparian oxbows of River Tisza in Csongrád county. The values were the following: Cr 88–95%, Ni 80–90%, Cu 73–93%, Zn 62–82%, Pb 90–97%, Cd 52–71%. The reducible Cr and Ni content of the floodplain soils measured by us is higher than that of the riparian oxbow sediments.

In conclusion, our measurement results in terms of the total element content of PTEs are in line with the results of researchers conducting studies in the area (UNEP/OCHA, 2004; BIRD et al., 2003; GOSZTONYI et al., 2010; LAKANEN & ERVIÖ, 1971). However, an important question remains unanswered namely the study

of arboreals. There has been data reported on the consequences of a mine accident on them in Aznalcóllar (SW Spain) more than 10 years ago (MADEJÓN et al., 2004).

Considering the fact that there was a significant difference (an increase) between the sampling results (2000–2017), it was proved that the 2006 flooding did not cause an increase in the PTE content except for only one location, Vásárosnamény (S2). However, this result was not due to a decrease in soil pH but to a rearrangement of the sediment structure.

Conclusion

The water and sediment contamination of River Tisza, which happened more than twenty years ago, has raised several questions that haven't been addressed ever since. One area of inquiry is what methods are needed to learn more about the contamination process and its expected consequences. Using the BCR sequencing method, adequate data can be obtained to determine the solubility status of PTEs. The result can be integrated into the regional information systems with measured soil pH values.

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